

DOE Chemistry Studies

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ICET



Mississippi State
UNIVERSITY

Work Reported On

- Neural Network Efforts
- Database Developments
- SRS Sludge Batch 5
- Gibbsite to Boehmite Transition
- Wednesday Evening Poster
 - Solubility Studies and Database Development
 - SRS DDA Experiments
 - Dissolved Salt Flow and Plugging Studies ca. 1999 - 2001

Hanford Tank Waste Operation Simulator - Neural Network Efforts

- Improvement of chemistry representation within model
- Currently runs entire campaign (2028) in 2 hours on laptop - 2 hour time steps
- Incorporate expressions based on SLE instead of wash & leach factors - 2 options
 - Neural Network
 - Calls to ESP engine
- Initial work was aimed at saltcake dissolution
- Calculations based on DBLSLTDB
- NeurOn-Line software (GenSym)
- Best representation was partial least squares with backward propagation
- Difficulties were encountered using sparse concentration range training sets

C-Farm Retrieval Schedule

Source Tank	Receiver Tank	Approximate Retrieval Start Date	Proposed Retrieval Technology
C-108	AN-106	12/15/2006	MSwR
C-109	AN-106	1/1/2008	MSwR
C-104	AN-101	3/1/2009	MSwR
C-107	AY-101	12/1/2010	MSwR
C-110	AN-106	1/1/2011	MSwR
C-112	AN-101	11/1/2012	MSwR
C-101	AY-101	3/1/2013	MRS
C-105	AY-101	4/1/2015	MRS
C-102	AZ-101	7/1/2015	MSwR
C-111	AN-101	9/1/2015	MRS

MSwR = Modified Sluicing with Recycle

MRS = Mobile Retrieval System

BBI data obtained 9/19/07

Charge reconciliation and molecular stream generation

ESP automation

Flowsheet development initiated

Retrieval Conditions

Mobile/vacuum retrieval system

- >30,000 gallons waste is retrieved at 22% solids by volume
- <30,000 gallons waste retrieved as a 2% slurry
- 400 gallons of slurry per batch, 8 batches per shift

Modified Sluicing

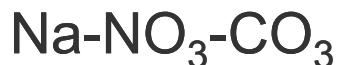
- Week 1 of operation transfer of 1% solids by volume
- thereafter increases to 6% until 20,000 gallons of waste remain
- 20,000 gallons < waste volume > 8,000 gallons retrieved at 2%
- 8,000 gallons <waste volume > 2693 gallons retrieved at 0.5% solids by volume
- 5400 gallons of waste per week

Path Forward

- Complete ESP automation
- Finalize flowsheet
- Transfer results to NeurOn Line - build extensive training sets
- Deliver data package to CH2M Hill
- Interfacing with HTWOS
- Testing and Recursion
- Go/No Go Decision on Neural network vs. OLI engine
- Generate more training data as necessary
- Begin training set for evaporator operations

Database Developments

- Saltcake core samples from Hanford SST's (with Dan Herting)
- Solubility studies on important salt systems



- Literature searches, data analysis, regressions
- DBLSLTDB double salt database for use in ESP 6.5
- Attempted to port to ESP version 6.7
- Ported to ESP version 7.0 V7DBLSLT

Rationale for Database Development Activities

- OLI Systems Inc.- 2 thermodynamic frameworks
 - Helgeson
 - Mixed Solvent Electrolyte (MSE)
- Discussions with OLI personnel have indicated that they will eventual focus entirely on MSE
- Concept was to port V7DBLSLT to the MSE Public Databank
 - Reduce ICET regression activities
 - Permanent repository for the ICET database

Quote obtained from OLI Systems Inc



Value Through Technology

Revised-2 Quotation for OLI Data Development
 Carbonates and sulfates have been deferred for this year.
 ICET's participation amount was increased for 2007 to reach a \$25,000 limit.

Date:	April 3, 2007	
Quotation To:	ICET at MSU	
Attention:	Dr. Jeff Lindner	
Data Service:	Transfer DBLSLTDB to OLI's MSE framework	
	42 days @ \$1,000 USD / day See breakdown on page 2	\$42,000
MSU Participation:	MSU performs all literature searches MSU collects all data in the form of regression input files	- \$17,000
	TOTAL	\$25,000
Notes:	<ol style="list-style-type: none"> 1) Deliverables from MSU include input files, and original source papers / reports 2) Deliverable from OLI will be an expanded MSEPUB databank, and a comprehensive set of QA spreadsheets 3) Payment schedule for OLI's data development: 50% of the funds will be invoiced at the project start, and the remaining 50% will be invoiced upon delivery of the data parameters. 4) ICET's participation amount discount has been increased by \$2,000 for 2007, and will be decreased by \$2,000 for any follow-up work in 2008 	



Value Through Technology

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Data Development Tasks for DBLSLTDB Transfer to OLI MSE Framework				
OLI Task No.	Priority		Task Days	Estimate Total Days
1		Literature Review (sources not already considered)	5	
2		Regression of parameters for missing binary aqueous systems	10	
	1	NaNO ₂	5	
	1	HNO ₂	5	
3		Regression of parameters for the following ternary systems....	18	
	1	NaOH-NaNO ₃	2	
	2	NaF-NaOH	2	
	3	NaF-Na ₃ PO ₄	2	
	3	NaF-NaNO ₃	2	
	3	Na ₃ PO ₄ -NaNO ₃	2	
	4	NaNO ₂ -Na ₂ CO ₃	2	
	4	NaNO ₂ -Na ₂ SO ₄	2	
	4	NaNO ₂ -NaOH	2	
	4	NaOH-Na ₂ CO ₃	2	
4		Verification of Predictions	5	
	2	NaF-Na ₂ SO ₄	1	
	2	NaOH-Na ₂ SO ₄	1	
	4	NaNO ₃ -Na ₂ SO ₄	1	
	4	NaNO ₃ -Na ₂ CO ₃	1	
	5	Na ₂ SO ₄ -Na ₂ CO ₃ (deferred)		
5		Final Testing QA, preparation of documentation	4	
	Total Days			42

These estimates are based on the 1/2/2006 quotation that was prepared by OLI's data development group.

This quotation is valid until June 30, 2007.

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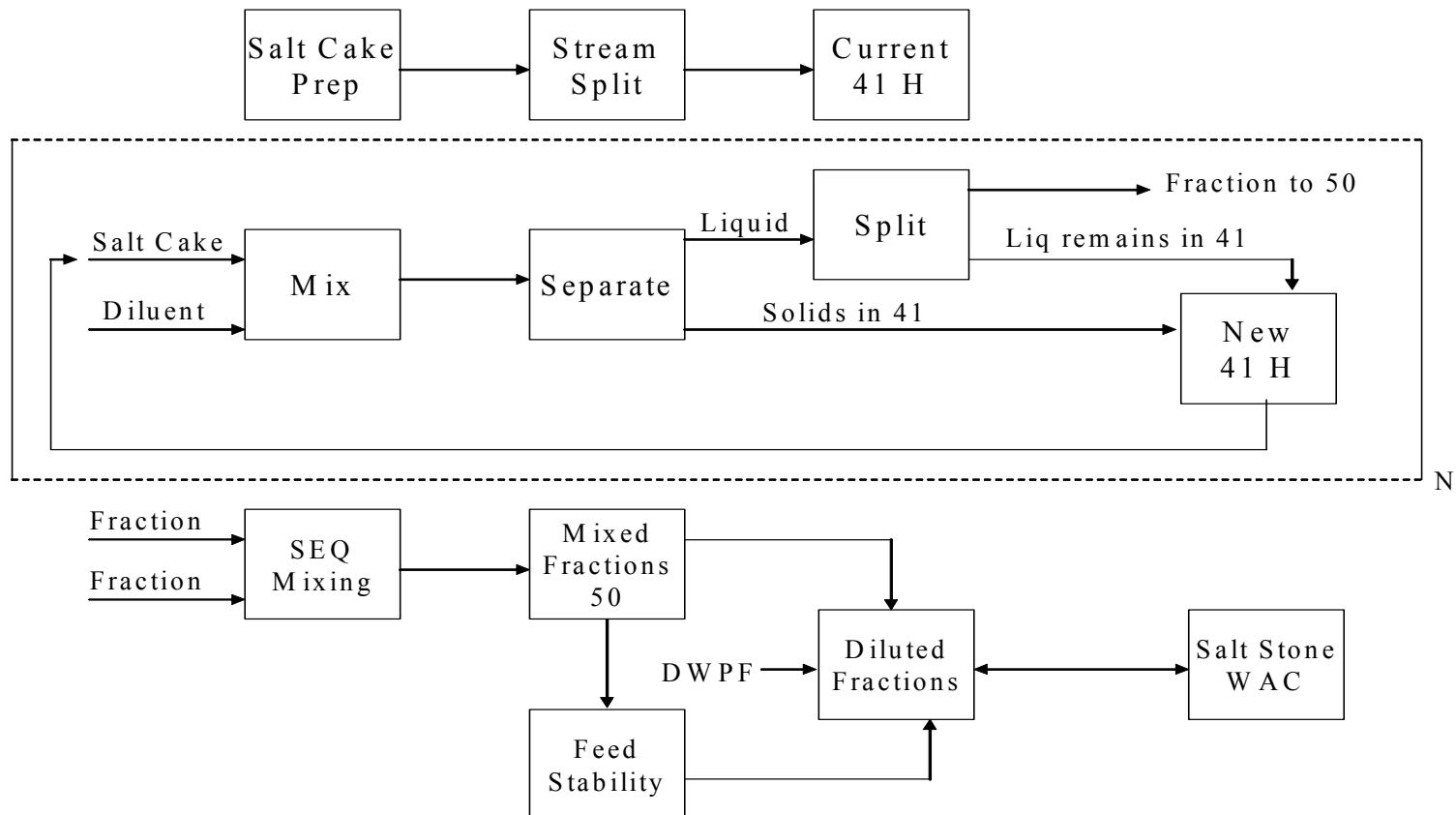
Subcontract Status

- Formally initiated June 12, 2007
- Data packages forwarded to OLI
 - Regression input files
 - Data compilation files
 - All applicable literature papers
- Work is on schedule for completions by 12/31/2007.
- Some systems had to be carried over to 2008 owing to subcontract limits at MSU.
- Additional data on Al, K, and Cs can be included in the 2008 work.

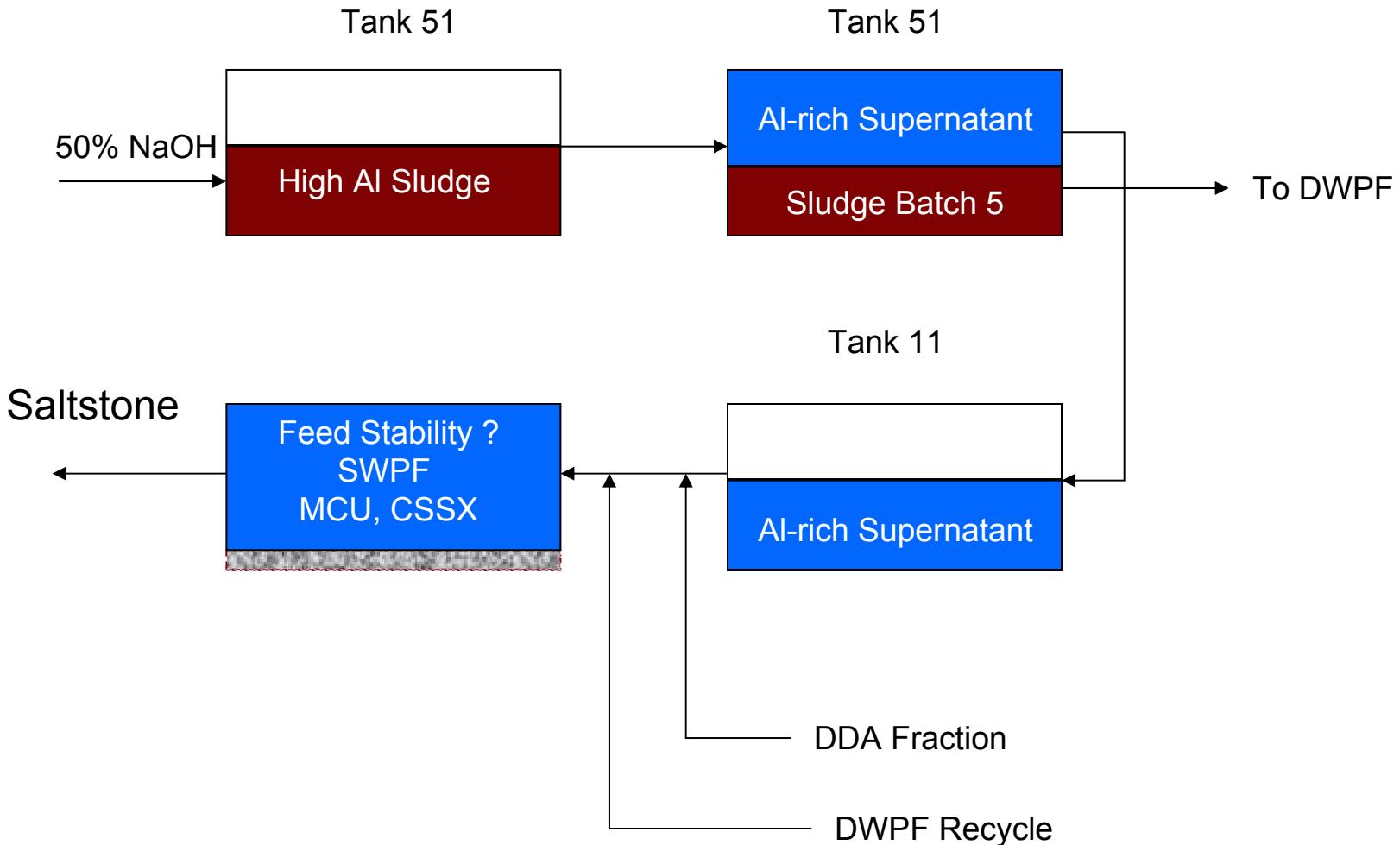
SRS Sludge Batch 5

- Discussions with Jeff Pike (early 2007) noted plans for leaching Al from sludge batch 5 and routing the leachate for possible blending with other streams (DDA fractions, DWPF Recycle, Effluent Treatment Facility)
- Stream blending is complicated by the potential for solids to re-precipitate thereby requiring additional water or caustic for further processing.
- Early studies (Poster) have indicated that solids re-precipitation is a function of the pH, temperature, and ionic strength of the 2 (or more) streams that will be blended.
- Additional solids formation may occur when specific ions react to form solids - mixing Al and Si in equimolar amounts in the presence of Na, OH, and carbonate or nitrate (sodium aluminosilicates).
- Our primary driver is to identify, in more detail, the factors that lead to solids re-precipitation.

Earlier ICET work involved the DDA processing of saltcake in Tank 41H



Overall Process - variables Temperature, Volume



ESP Calculations

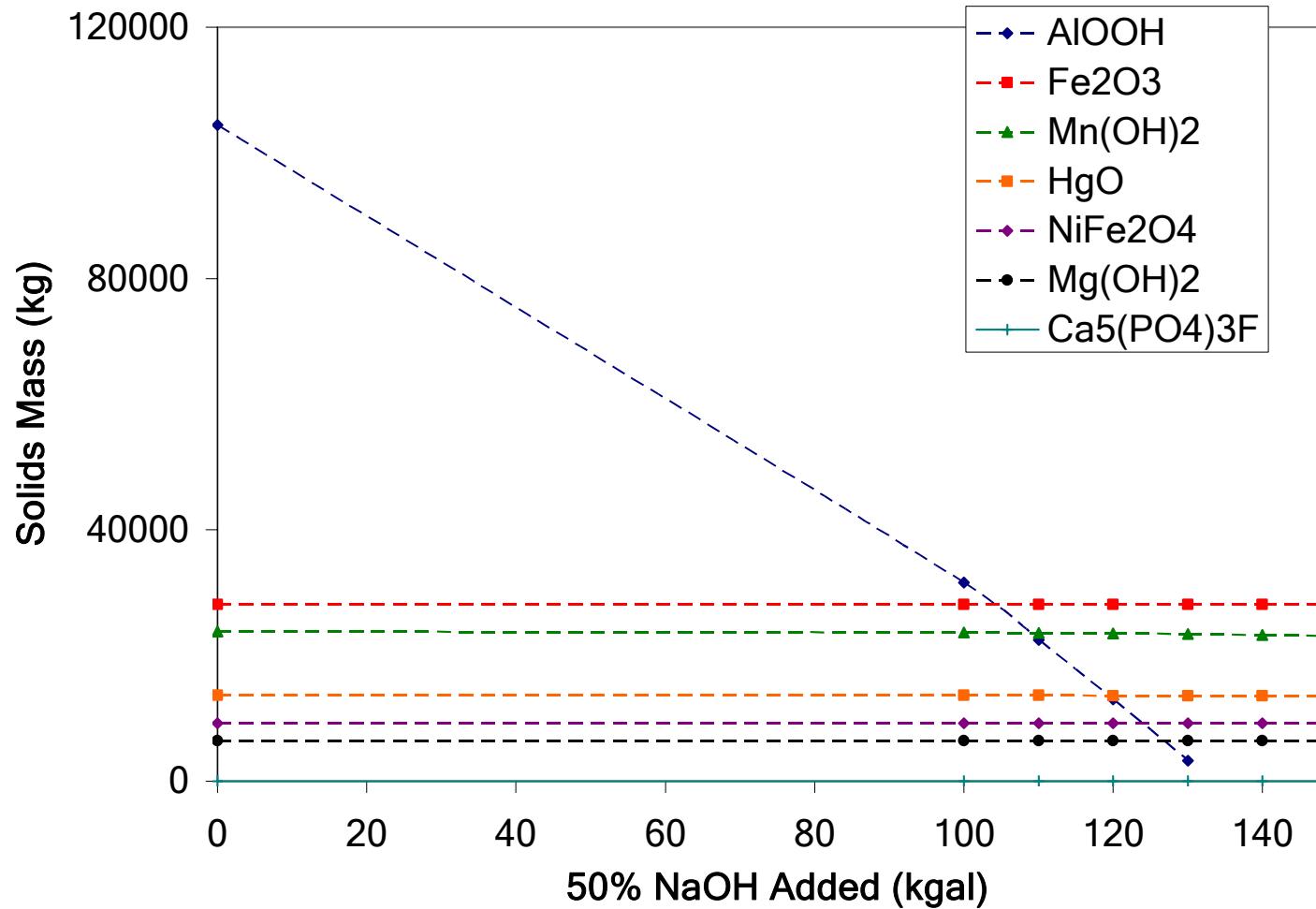
- Started with HM sludge simulant - Ketusky, E., "High Level Waste System Impacts from Acid Dissolution of Sludge" CBU-PIT-2005-00260R1, Westinghouse Savannah River Company, Aiken, SC (2005).
- Tuned to attain approximate 29% by weight Al
- Set density
- Databases Employed
 - V7DBLSLT
 - Corrosion
 - Jeff (AlOOH with temperature range 34-200°C)
 - Zeolite

ESP results are in agreement with SRS characterization

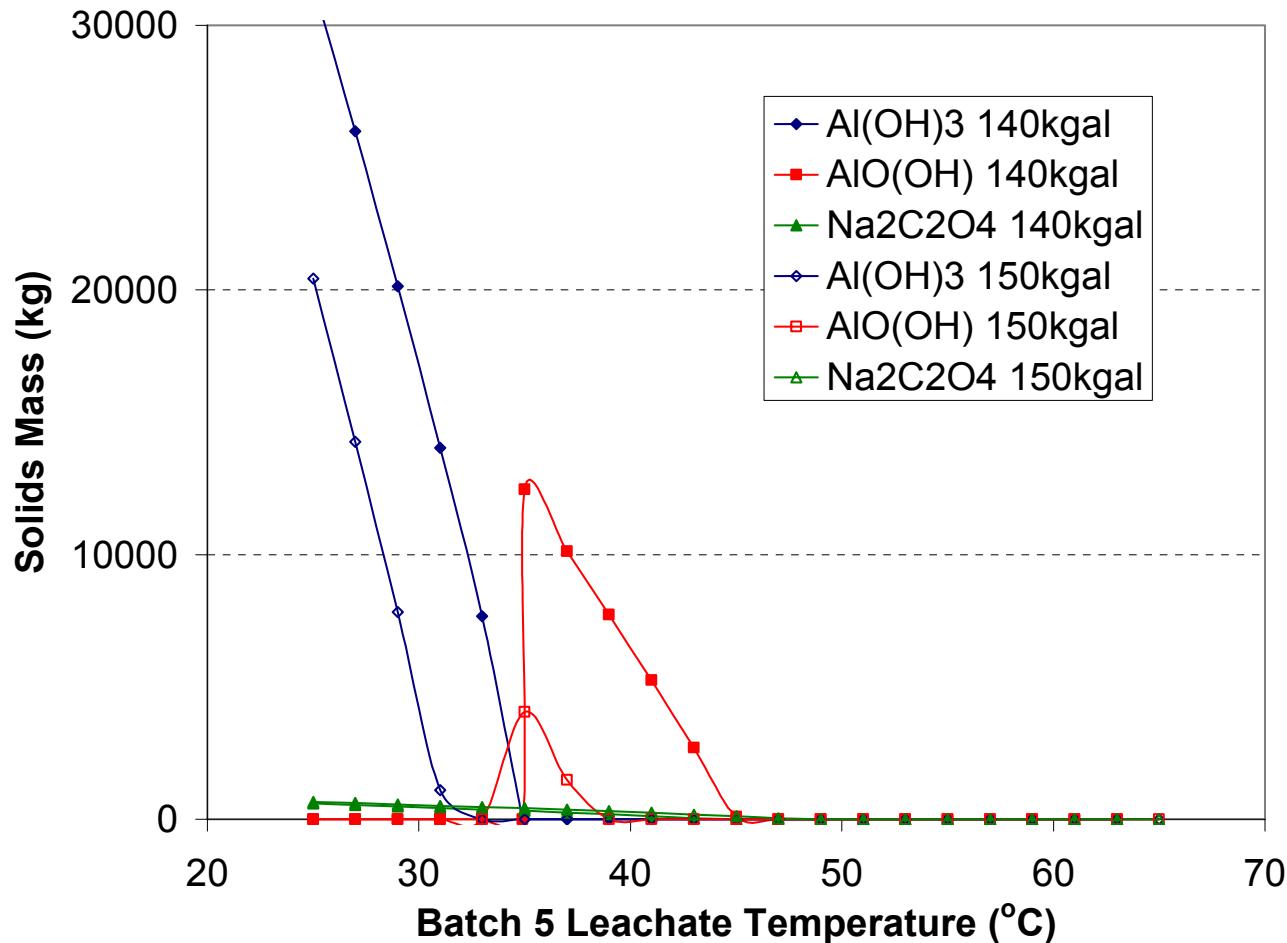
Pike, J. A., and J. M. Gillam, "Flowsheet for Aluminum Removal from Sludge Batch 5." LWO-PIT-2007-00042, rev. 1, Washington Savannah River Company, Aiken SC, Sept 2007

	SRS Data	ESP	Aqueous Phase Concentration, M	SRS Data	ESP
Aqueous Phase					
Vol, gal	4.68E+05	4.71E+05	Na	1.090	1.064
Sp G	1.03	1.04	NO2	0.470	0.466
Mass Aq, kg	1.83E+06	1.85E+06	NO3	0.300	0.297
Al, kg	1000	1029	"free" OH	0.100	0.142
pH		12.33	Cl	0.007	0.006
Ionic Strength		1.10	SO4	0.024	0.024
Solid Phase			F	0.002	0.002
Vol, gal	2.07E+04	1.34E+04	CO3	0.037	0.037
Sp G	2.40	3669.95	AlO2	0.021	0.021
Mass Insol solids, kg	1.88E+05	1.86E+05	C2O4	0.005	0.005
wt% Al in solids	25.30	25.29	PO4	0.001	0.001
Al kg as elemental)	4.75E+04	4.70E+04	K	0.003	0.003
Other Components, kg	1.40E+05	1.39E+05			
Total Tank					
Total Vol, gal	4.89E+05	4.84E+05			
wt% insoluble solids	9.30	9.14			
Total Mass, kg	2.02E+06	2.03E+06			

Addition of 130+ kgal of 50% NaOH is expected to dissolve the majority of the solid phase aluminum ($T=50^{\circ}\text{C}$)



Cooling of the leachate stream (OLI Inc. Stream Analyzer) will result in the re-precipitation of Boehmite or Gibbsite and Sodium Oxalate



Initial Attempts at Blending the 51H Leachate

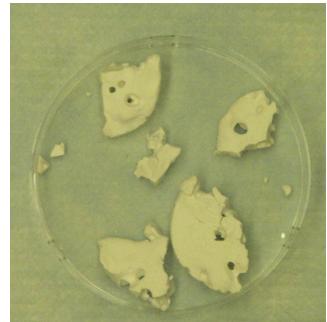
	Cooled leachate in 11	Leachate & frac 1 mixed	Leachate,1&2 DDA mix
Aqueous			
% Water by Wt.	75.79	67.06	62.64
pH	14.77	14.78	14.68
Ionic Strength	5.69	7.65	8.69
Solids			
Al(OH) ₃	1.69E+04	3.01E+04	4.12E+04
CaFe ₂ O ₄	2.59E-03		
Fe ₂ O ₃	3.60E-01	3.14E-01	3.02E-01
HgO	1.64E+01		
Mg(H) ₂	7.75E-06	2.47E-06	
Na ₂ C ₂ O ₄	4.64E+02	5.11E+02	7.57E+02
% solids by wt	0.63	0.67	0.65

- Predictions with addition of the DWPF recycle stream are in progress
- Concerns:
 - NAS formation
 - Large chemistry model

Initial Results Batch 5 Leaching and Blending

- Good agreement has been observed for the base composition of Batch 5 in tank 51.
- Addition of 130kgal. of 50% NaOH at 50°C is necessary for Al dissolution.
- Improved feed stability is observed with larger volume additions - the resulting leachate can be cooled to lower temperatures.
- Comparisons with lab experiments being conducted at SRNL are planned.
- It appears possible to blend DDA fractions from 41H with the leachate only producing small quantities of re-precipitated solids.
- Studies using the DWPF recycle stream are in progress.

Gibbsite to Boehmite Transition

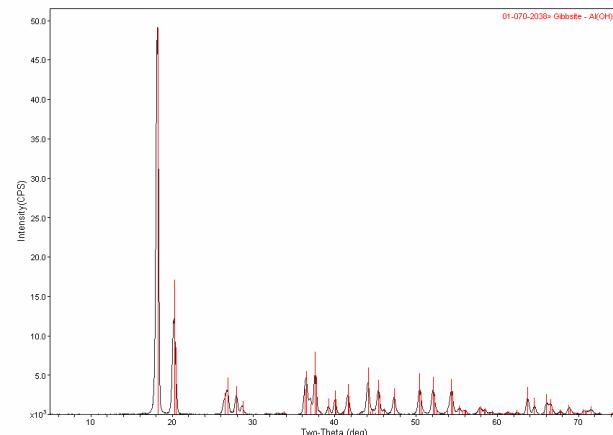
$$\text{Al(OH)}_3 \rightarrow \text{AlOOH} + \text{H}_2\text{O}$$


- Form of aluminum has implications on sludge washing/leaching (HLW/LLW separations).
- Al(OH)_3 soluble in NaOH AlOOH exhibits slow kinetics.
- Transition Observed at 150°C - Gong, X., et al., "Gibbsite to Boehmite Transformation in Strongly Caustic and Nitrate Environments." Industrial and Engineering Chemistry Research, 42, 2163-2170, (2003).
- Lowered Temperature Range, examined effect of caustic - Ruff, T. J., "Aluminum Chemistry and its Implications on Pretreatment and Disposition of Hanford Waste," MS Thesis, Swam School of Chemical Engineering, August, 2007.
- Currently Extending Range to <=100°C.

Experimental

- Almatis C-333 gibbsite concentration 6.41 molal for all experiments
- Conditions
 - 1.5, 3m NaOH, 50-150°C range
 - 1.5m NaOH 0.5m NaNO₂ & NaNO₃
 - Dry, low pressure (allowed complete evaporation)
 - Wet, high pressure (sealed containers PCT vials)
- Expose to desired temperature for prescribed period of time in oven. Remove, grind, filter, wash, and analyze.
- Thermogravimetric Analysis

Qualitative XRD

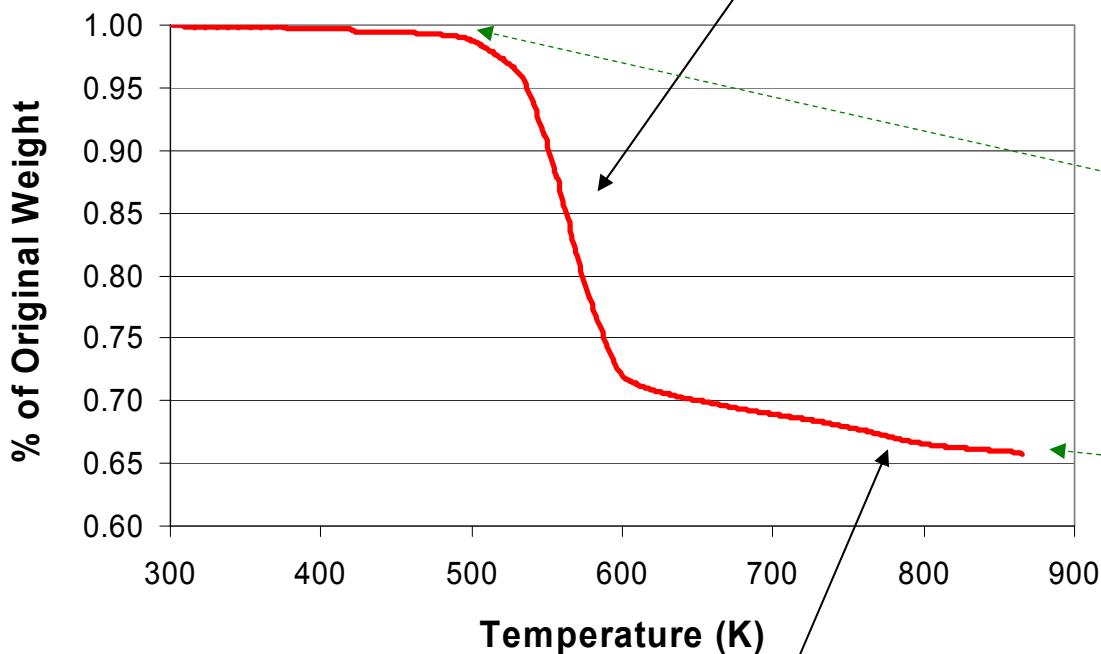


Composition Calculation from TGA Data



200-400°C

23.1% wt. loss)



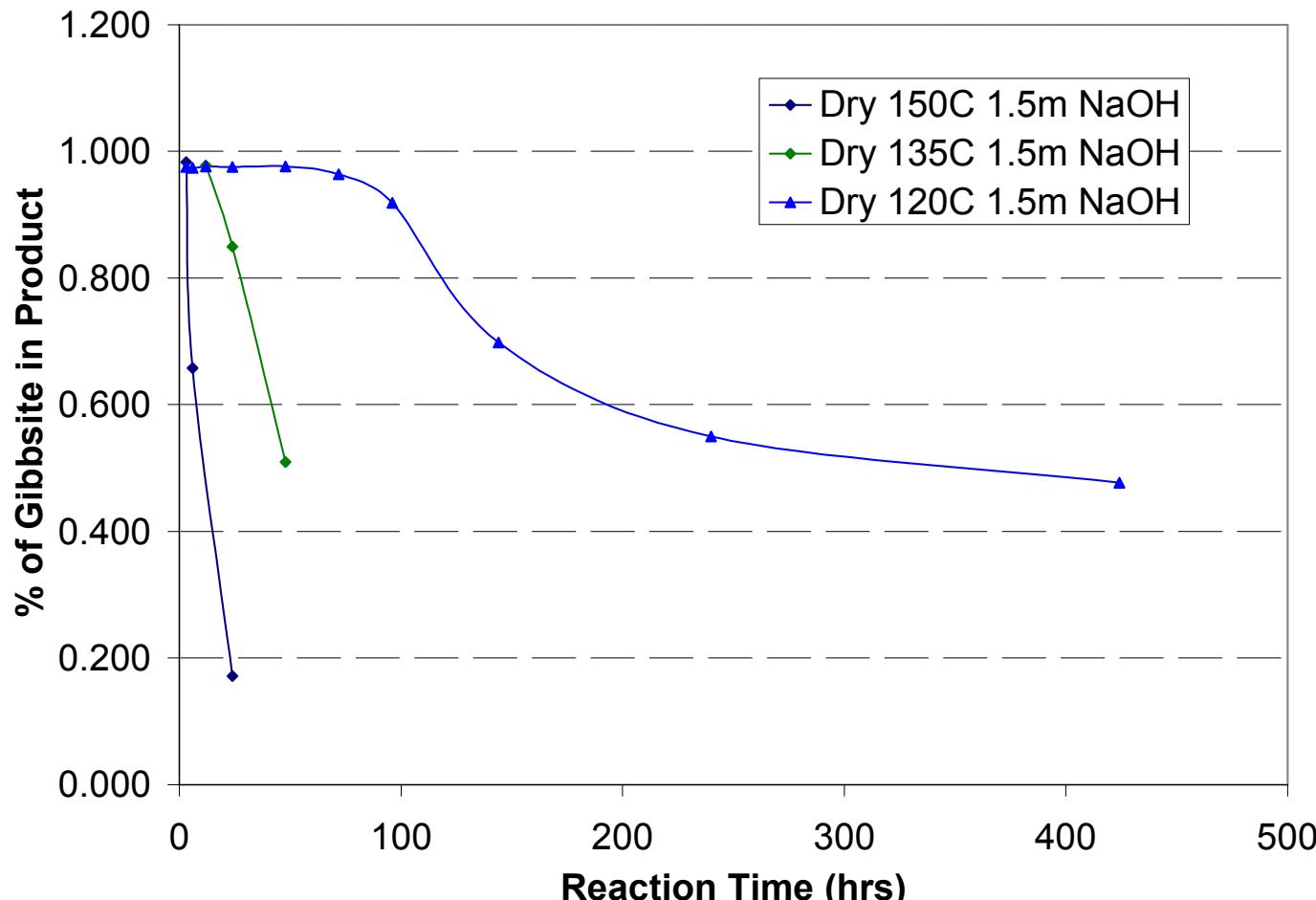
The Almatis Gibbsite 34.6%
wt.loss (34.64% theo.)

$$x_{gibbsite} = \frac{\left[\frac{w_i - w_f}{w_i} - \frac{1}{2} \frac{MW_{H2O}}{MW_{boeh}} \right]}{\left[\frac{3}{2} \frac{MW_{H2O}}{MW_{gibb}} - \frac{1}{2} \frac{MW_{H2O}}{MW_{boeh}} \right]}$$

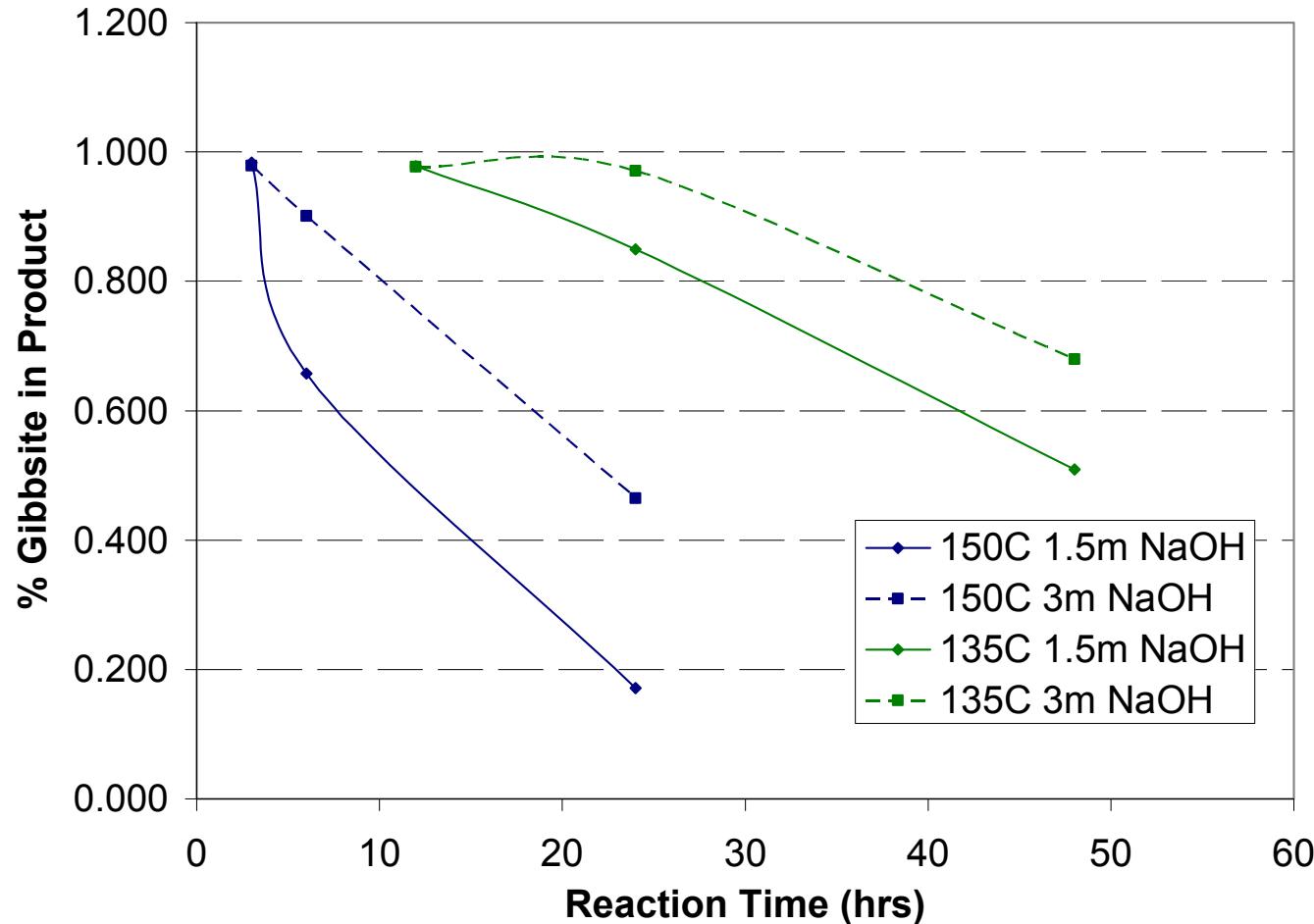
w_i = sample weight
after 150 °C hold
time

w_f = sample weight
at end of program

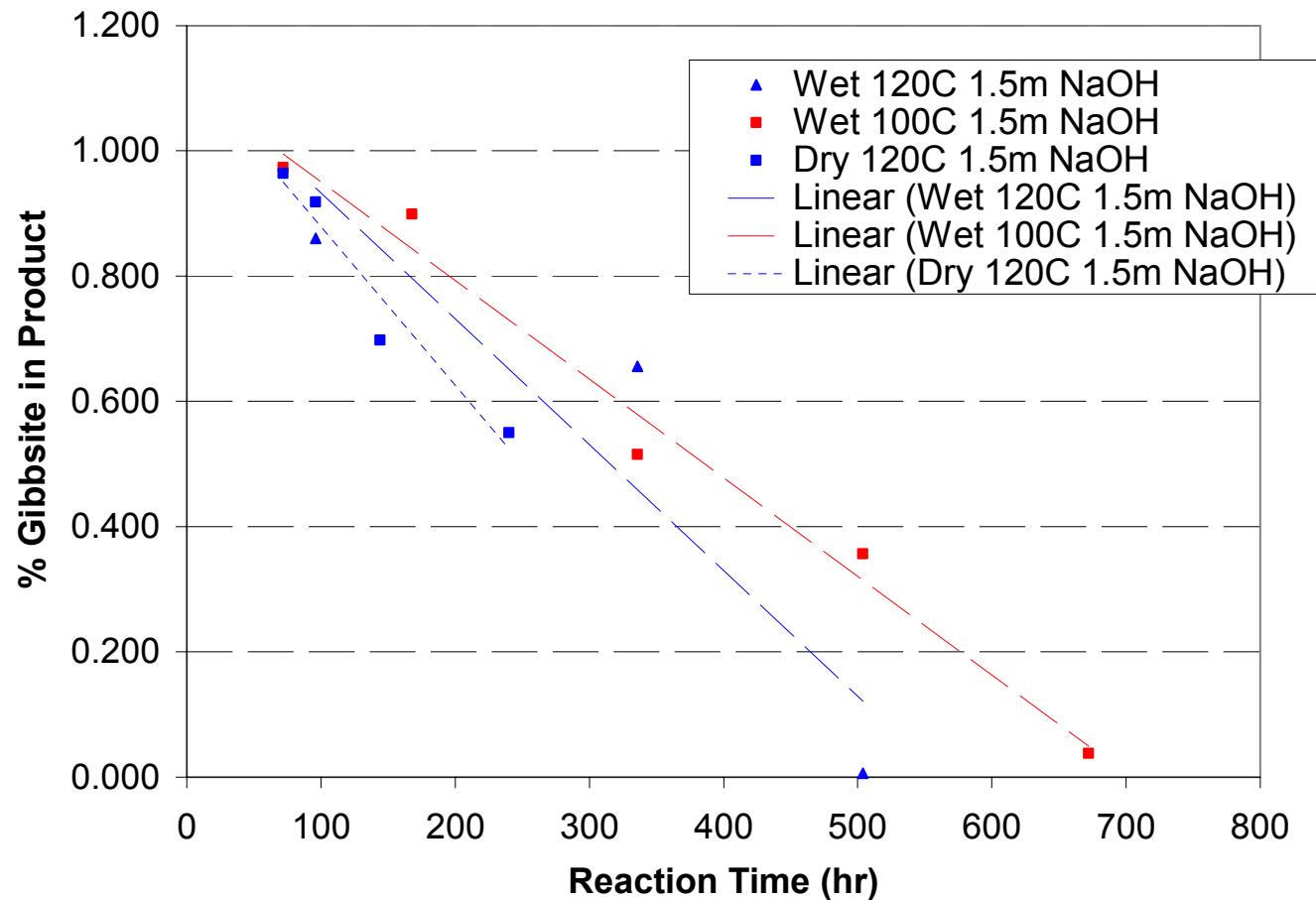
Conversion of Gibbsite to Boehmite is rapid at T>135°C reduced at 120°C



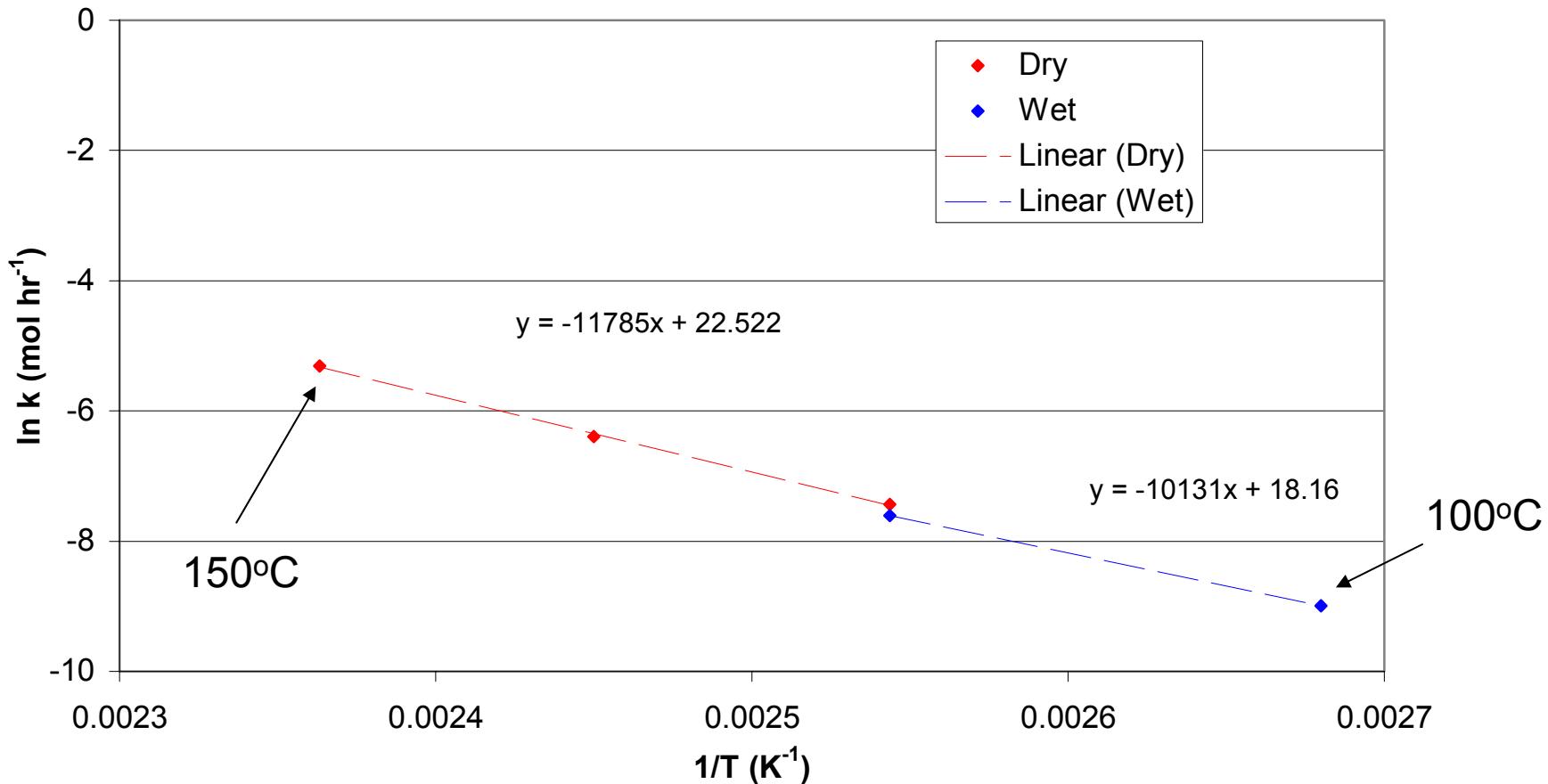
At 135 and 150°C (Dry Conditions) an increase in [NaOH] does not significantly effect the rate of reaction once started



Initial Data Indicates Little Difference in Reaction Rates for Dry or Wet Conditions



Activation Energies for the Wet and Dry Experiments are, within experimental error, the same (84.2 and 97.9 kJ/mol)

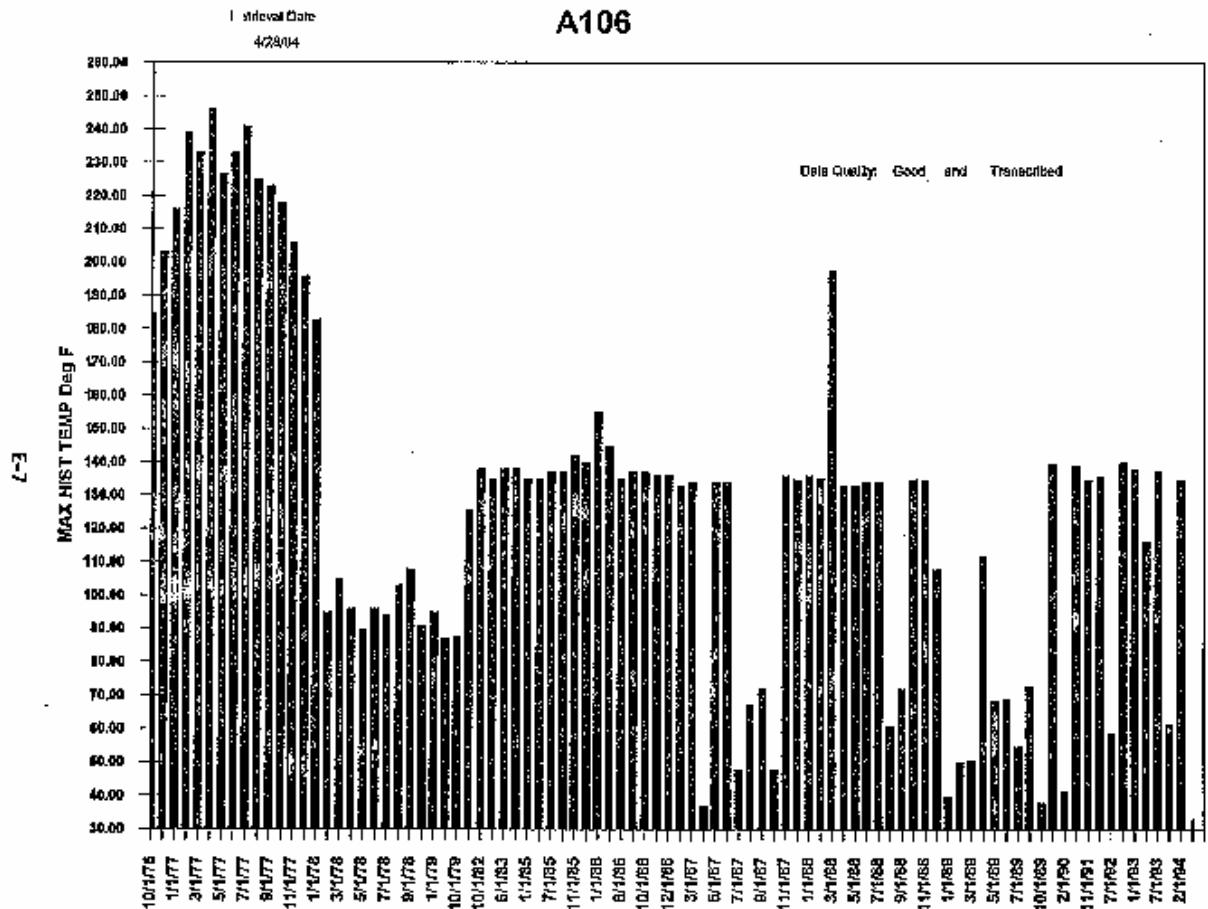


Correlation to Historical Waste Conditions - Flanagan, B. D., "Maximum Surface Level and Temperature Histories for Hanford Waste Tanks," WHC-SD-WM-TI-591, rev. 0, Westinghouse Hanford Corporation, Richland WA (1994).

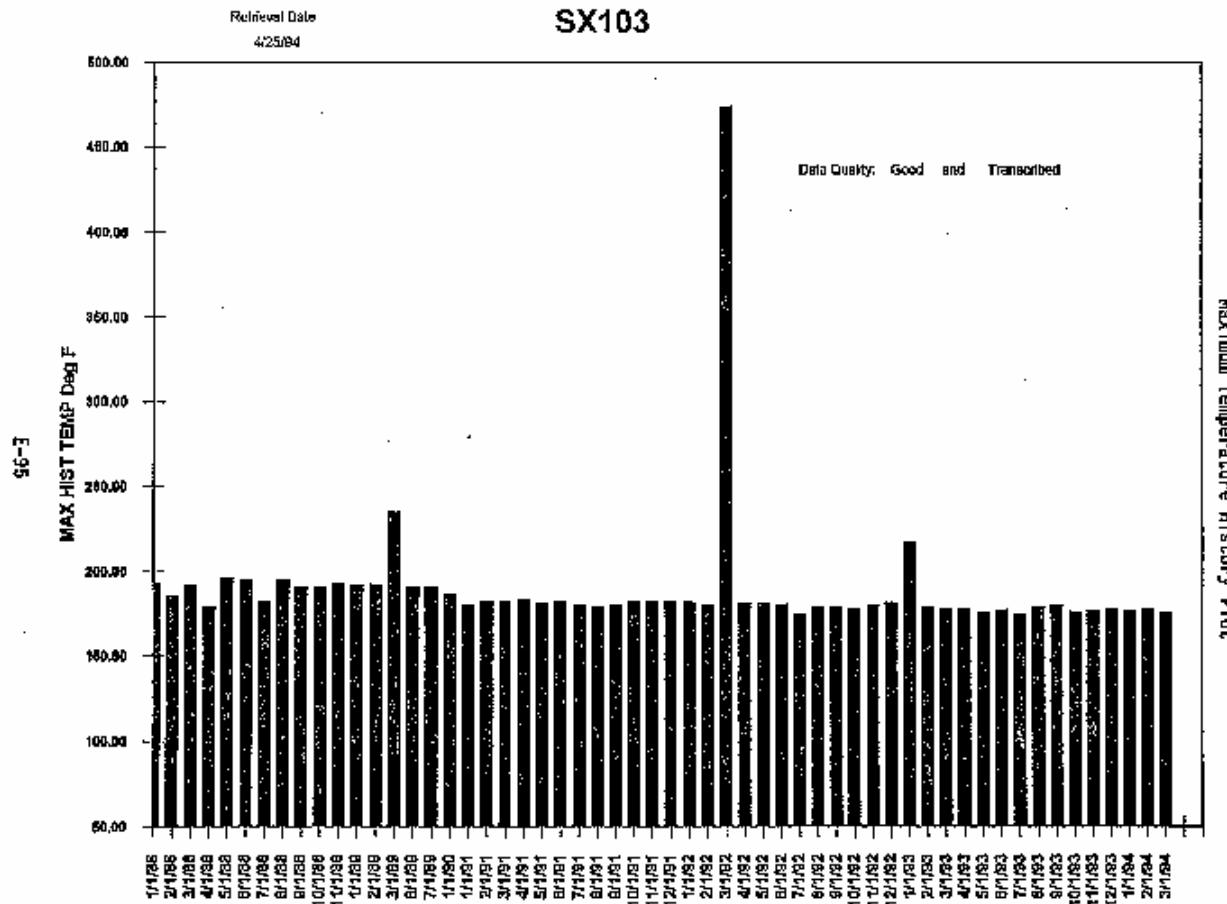
Maximum Temperatures in °C

A-101	204	BY-104	114	S-101	149	TX-105	114
A-102	216			S-104	149		
A-103	149			S-107	116		
A-104	221			S-110	116		
A-105	163						
A-106	306			SX-101	160	SX-110	154
				SX-102	100	SX-111	160
AX-101	127			SX-103	107	SX-112	157
AX-102	121			SX-104	149	SX-113	124
AX-103	166			SX-105	166	SX-114	168
AX-104	160			SX-107	199	SX-115	127
AZ-101	102			SX-108	160		
AZ-102	116			SX-109	146	SY-101	127

From Flanagan, B. D., WHC-SD-WM-TI-591,rev. 0,
Westinghouse Hanford Corporation, Richland WA (1994).



From Flanagan, B. D., WHC-SD-WM-TI-591,rev. 0,
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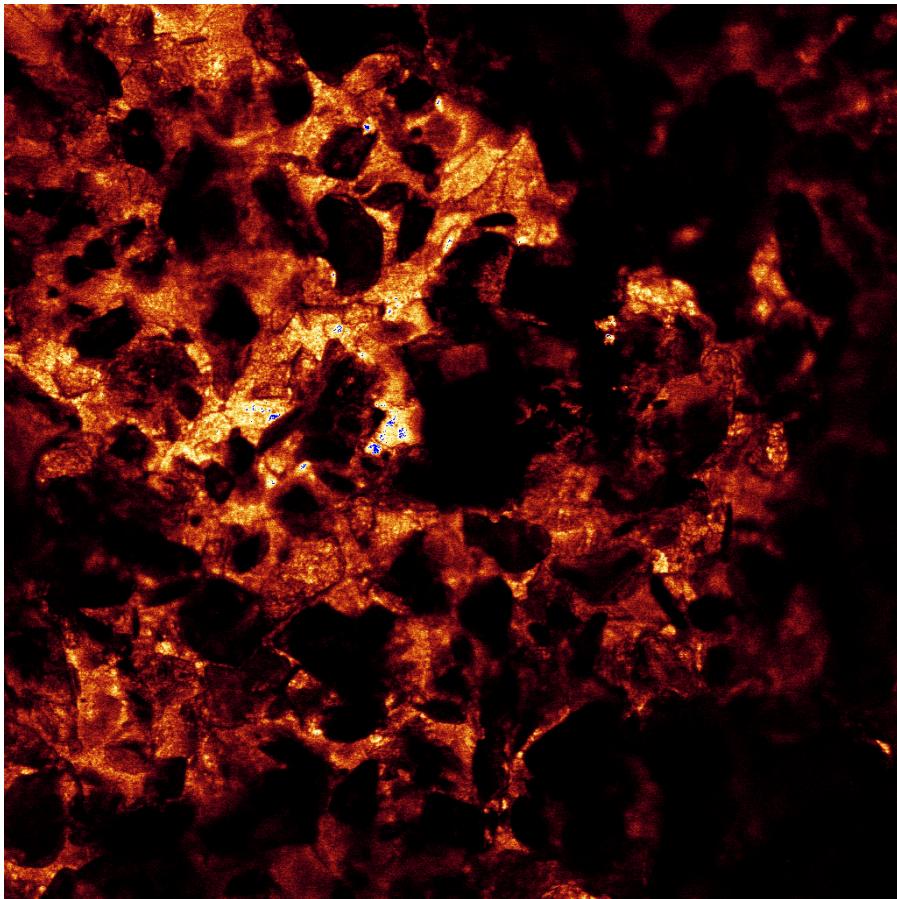
Comments on the Gibbsite to Boehmite Transitions

- The TGA method is a rapid technique to quantify fractions of Al(OH)_3 and AlOOH
- Interferences are likely with real waste samples containing iron (similar solid phase transitions)
- The transition can occur as low as 100°C.

Temperature (°C)	150	135	120	100
mol/hr=r	4.95E-03	1.67E-03	5.90E-04	1.21E-04

- Higher caustic loadings extend the induction period (delayed evaporation) but have little effect on the rate of reaction.
- Some historical temperature data is available to obtain a better estimates of Boehmite weight fractions

Questions



Laser Confocal Microscope
Image of Saltcake